Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 36 (2010) 2253–2257
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Short communication

Sintering process and high temperature stability investigation for nano-scale CaB_6 materials

Lin Zhang *, Guanghui Min, Huashun Yu, Hui Yu

Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials (Ministry of Education), Shandong University, Jinan 250061, PR China

Received 27 January 2010; received in revised form 2 February 2010; accepted 7 May 2010
Available online 25 June 2010

Abstract

Calcium hexaboride (CaB_6) polycrystalline was prepared from its nano-scale powders using vacuum hot-pressing method under 1750 °C, 32 MPa for 5 min. SEM, FESEM and AFM were employed to observe morphology and compared with its bulk material sintered under 1550 °C. Observations showed the structure of the nano-scale CaB_6 bulk has the regions with high and low compactness degree due to CaB_6 nanometer powder aggregations. The hardness, bending strength and fractural toughness were 79.7 HRA, 198.7 MPa and 3.73 MPa $m^{1/2}$, respectively, better than those of CaB_6 micron-polycrystalline sintered under the same sintering parameters. DSC and TG were tested to investigate high temperature stability. Only one exothermic peak (1117.2 °C) appeared in nano-polycrystalline which began at 1080 °C and area was −167.7 J/g, showing its stability is much better than CaB_6 nano-micron composite polycrystalline and micron-polycrystalline.

Keywords: Calcium hexaboride; Nano-scale powder; Vacuum hot-pressing; Mechanical property; High temperature stability

1. Introduction

Calcium hexaboride (CaB_6) has very important values both in research and application due to its good combination of mechanical properties, chemical stability and unique physical properties [1–4], which show a potential application in advanced instruments industry. In order to further probe the natures of this material, the recent research focused on the physical properties of its ultrafined or nano-scale material. Superfine [5] and submicron CaB_6 cubic particles [6], CaB_6 nanowires [7,8] have already been synthesized. It was discovered that the physical properties such as magnetic performance and optical property [9] are different from its micron-powders, which highlighted the research significance of nano-scale CaB_6.

In this paper, the vacuum hot-pressing method was employed to prepare CaB_6 polycrystalline bulk from its nano-powders. The sinterability of nano-powders was analyzed and compared with CaB_6 micron-powders and its nano-micron composite powders. High temperature stability of polycrystalline bulk material was also tested and analyzed in this work.

2. Experimental procedure

Nanometer CaB_6 powders (average particle size 80 nm), micron-scale CaB_6 powders (average grain size 5 μm) were used as raw material in this study, which were prepared by ourselves (Boride Research Group of Shandong University, P. R. China). Their mixture powders were mingled by planetary high energy mill (model: QM-1SP(2L)) using carnelian balls as media for 10 h at a rotate speed of 380 rpm.

A high purity graphite mould whose inner diameter is Ø 40 mm was used to fill nano-scale CaB_6 powders and then was put into vacuum hot-pressing sintering furnace which working vacuum degree is 6.67×10^{-2} Pa. The powders were heated by high pure graphite heater at a rate of 16 °C/min to the schedule temperatures 1550 and 1750 °C. After 32 MPa pressure was brought to bear on powders for 5 min, the material was cooled with furnace. In order to compare the high temperature stability, the polycrystalline bulks of CaB_6 micron-powders and CaB_6 nano-micron composite (nanometer powders content was 10 wt.%) were pressed under the same parameters.

Crystal slicing machine was used to cut one polycrystalline bulk to five samples which size were 30 mm × 4 mm × 3 mm. The samples were polished by different sizes boroncarbide (B_4C) powders as abrasive. Atomic force microscope (AFM, model: AFM-IIa) and scanning electron microscope (SEM,

* Corresponding author. Tel.: +86 531 88395639; fax: +86 531 88395639.
E-mail address: zhanglin2007@sdu.edu.cn (L. Zhang).

0272-8842/$36.00
doi:10.1016/j.ceramint.2010.06.005

model: Hitachi S-2500) were used to examine microstructure. Field emission scanning electron microscope (FESEM, model: JSM-6700F) was employed to observe fractural morphology. Differential Scanning Calorimetry (DSC, model: Netzsch DSC404C) was used to analyze the oxidation behavior with elevated temperature.

The compactness degree was tested by pycnometer method according to Archimedes law. Hardness values were achieved by Rockwell hardness tester (model: HRS-150) with load 150 kgf and eight points of each sample were tested to get the mean value. Bending strength and fractural toughness were measured by portal type microcomputer control electron universal tester (model: CMT5105). All above mechanical properties data for one bulk measured from its five samples in order to reduce the experimental error.

3. Result and discussion

Fig. 1 showed the SEM images of CaB_6 polycrystalline bulk which were made of nanometer powders sintered at different temperature. A number of pores were observed in CaB_6 nano-scale polycrystalline at 1550 °C as shown in Fig. 1(a). The average size of the large pores was about 100 μm in length and 20 μm in width. Almost no nano-particles could be found in the large pores, and the pores became smaller in dense area. The high magnification observation showed the polycrystalline still has the powder-like morphology, which indicated that sintering has not fully completed at 1550 °C.

The microstructure of CaB_6 nano-scale polycrystalline changed significantly when the temperature increased to 1750 °C. SEM observation (Fig. 1(b)) showed the microstructure consisted of the regions with high and low compactness degree. With the elevation of sintering temperature, the edges circularization of pores occurred due to the diffusion of atoms. From Fig. 1(c), the large pores left in samples sintered at 1550 °C were divided by neck growth and tangled into network-like structure. And it was obvious that the tiny pores in dense area closed and shrank, so the densification microstructure achieved eventually as shown in Fig. 1(d).

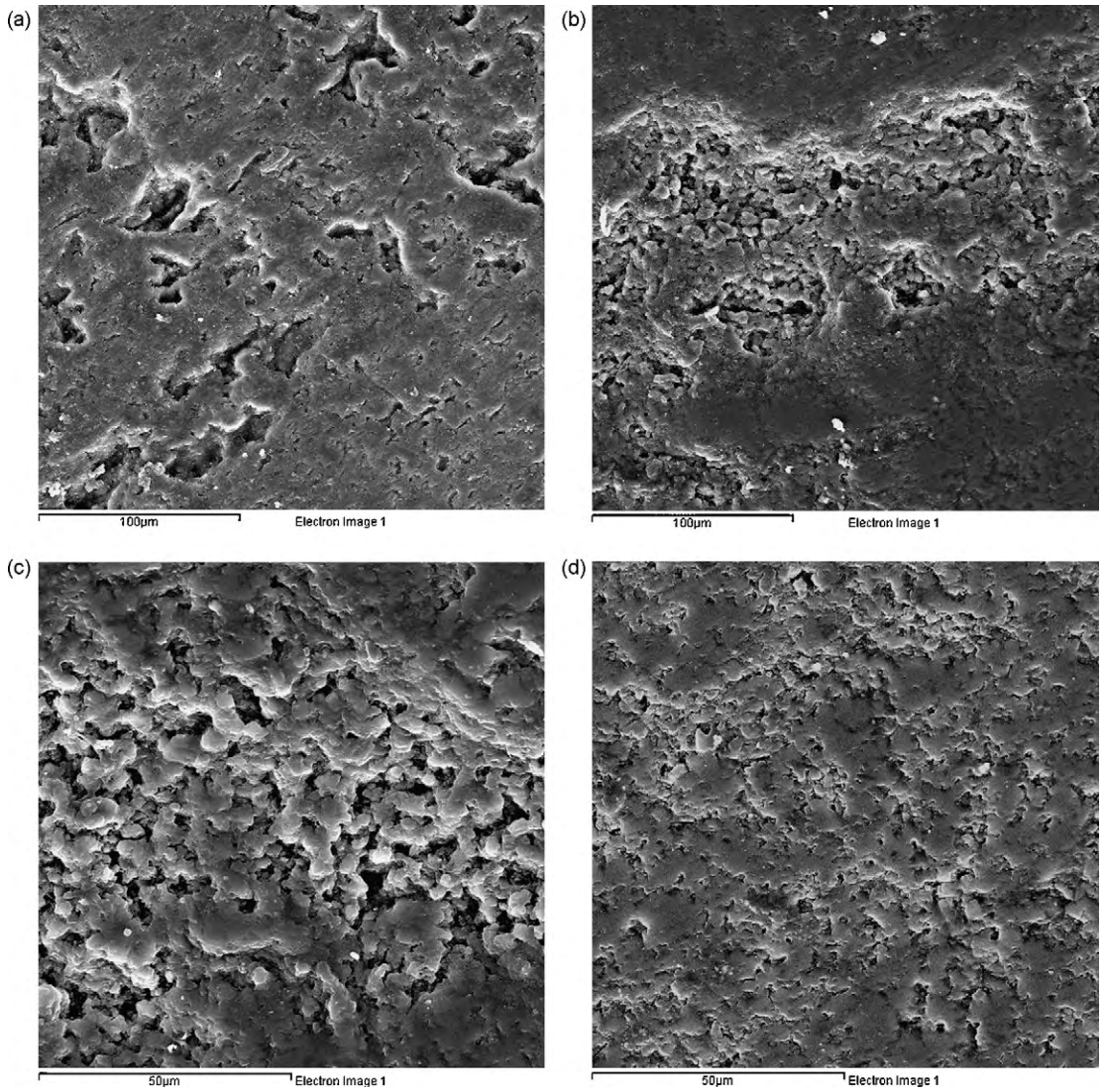

Fig. 1. SEM of morphologies of CaB_6 polycrystalline made of nanometer powders sintered under different temperatures: (a) 1550 °C, (b)–(d) 1750 °C.